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Surface Kinetic Model for the Fractionation of Trace Elements and Isotopes in Calcite Precipitated from Aqueous Solution

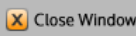
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TITLE: Surface Kinetic Model for the Fractionation of Trace Elements and Isotopes in Calcite Precipitated from Aqueous Solution

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CURRENT SECTION/FOCUS GROUP: Paleooceanography and Paleoclimatology (PP)

CURRENT SESSION: PP18. Mechanisms Controlling the Incorporation of Paleoproxies into Host Minerals: Contributions From Molecular-Scale Approaches

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Title of Team:

ABSTRACT BODY: The isotopic and trace element concentrations in calcite and other carbonate minerals form the basis for several paleoceanographic and paleoenvironmental indicators. The chemical and isotopic composition of natural calcites is determined by a combination of equilibrium partitioning and kinetic fractionations. Currently there is no general model that describes when equilibrium applies and how kinetic effects depend on the circumstances and rates of mineral growth. A useful approach is to separate the growth of calcite from aqueous solutions into forward (f) and backward (b) reactions, and to consider the mechanisms and fractionations that may be associated with each. We are evaluating a model where the net precipitation rate of calcite (R_p) is expressed as the difference between a forward rate (R_f) and a backward (dissolution) rate (R_b). Dissolution is approached only as $R_p/R_b \rightarrow 0$. Much natural calcite, including biogenic, forms under conditions where $R_p \gg R_b$, hence the isotopic and trace element partitioning is strongly influenced by the kinetics of the forward reaction. Assuming that there are kinetic fractionations associated with the forward and backward reactions, a simple model can be developed for the dependence of calcite composition on precipitation rate. This model can explain most available experimental data on Ca and O isotopes, as well as Sr/Ca and Mn/Ca in calcite, and can be used to infer the behavior of other trace and minor elements. The critical parameter in applying the model is the value of R_b which to first order can be estimated from mineral dissolution rates, but apparently is not a constant, but instead varies with solution chemistry, especially at saturation conditions close to equilibrium. The surface kinetic model requires three parameters that are measurable experimentally and potentially also predictable from molecular dynamics simulation approaches. In this way it differs from the surface entrapment model of Watson (2004) which requires six parameters that cannot be independently measured. The next step in understanding the controls on calcite chemistry is to investigate the dependence of R_b (i.e., the surface molecular exchange rate) on precipitation conditions and mechanisms, and to quantify the interplay between the presence of impurities in calcite and the exchange rate. These issues are being addressed with a combination of experiments, studies of natural systems, and MD simulations.

INDEX TERMS: [0419] BIOGEOSCIENCES / Biomineralization, [4912] PALEOCEANOGRAPHY / Biogeochemical cycles, processes, and modeling, [4924] PALEOCEANOGRAPHY / Geochemical tracers, [1042] GEOCHEMISTRY / Mineral and crystal chemistry.

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